

PATENT SPECIFICATION

1,035,566

1,035,566



Date of Application and filing Complete
Specification: September 18, 1964.

No. 38239/64

Application made in Japan (No. 50990) on September 21, 1963.

Complete Specification Published: July 13, 1966.

© Crown Copyright 1966.

Index at Acceptance:—C3 P (1A, 1C6B, 1C9, 1C14B, 1C16A, 1C16C, 1C18, 1C20B, 1C20D1, 1D1A, 1D1B, 2A, 2C6B, 2C13C, 2C14B, 2C16A, 2C16C, 2C18, 2D1A, 2K8, 4A, 4C6B, 4C13C, 4C14B, 4C16A, 4C16C, 4C20B, 4C20C, 4C20D1, 4C20D3, 4D3B1, 4K10, 7A, 7C6B, 7C13B, 7C13C, 7C14B, 7C16A, 7C16C, 7C18, 7D2A1, 10A, 10C2, 10C5, 10C6B, 10C8B, 10C8C, 10C9, 10C12B, 10C12X, 10C13A, 10C13B, 10C13C, 10C14B, 10C16A, 10C16C, 10C17, 10C18, 10C20B, 10C20C, 10C20D1, 10C20D3, 10D1A, 10D4A, 10FX, 10K4, 10P1D, 10P1E1, 10P1E3, 10P1E4, 10P3, 10P4B, 10P6H, 10T2B); B2 B (4E1A1, 4E1BY, 4E1CI, 4E2D, 4E2Y, 4E3D, 4E4X, 4E6C, 4E7A3, 4E7AY, 4E7B1, 4E7B3, 4E7B4, 4E7B5, 4E8D, 4E8X, 4E9C, 4E9E, 4E9G, 4E9J, 4E9M, 4E9P, 4E9Q2, 4E9Q3, 4E9Q4, 4E9Q5, 4E9Q6, 4E9Q7, 4E9Q8, 4E9QX, 4E9QY); C3 F (2A, 2F, 2H, 3A, 3E, 3G, 3L, 3M, 3R); C4 X11.

Int. Cl.:—C 08 f 29/16 // B44d, C08b, C09k.

COMPLETE SPECIFICATION

NO DRAWINGS

Coating Composition

PATENTS ACT, 1949

SPECIFICATION NO. 1,035,566

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 3rd day of May 1968, this Specification has been amended under Section 33 in the following manner:-

Page 7, delete line 20, insert

"We are aware of Patent No. 1,018,269 which claims a dispersion comprising 5 to 60% of particles of a fluorocarbon polymer having a molecular weight of 2,000 to 10,000, 40 to 95% of a thermosettable or thermoplastic resin, 0 to 30% of particles of polytetrafluoroethylene having a molecular weight above 500,000 and a solvent for the said resin, the percentages being based on the total weight of polymers and resin solids, a method of forming an adherent low-friction coating on a substrate which comprises applying thereto a dispersion as aforesaid and drying it, at ambient temperature when the said resin is a thermoplastic resin and at an elevated, curing temperature when the said resin is a thermosettable resin, and substrates provided with an adherent, low friction coating by this method, and we make no claim to such a dispersion, method, or substrate. Subject to the foregoing disclaimer, what we claim is:—"

Page 7, delete lines "125, 126 and 127"

THE PATENT OFFICE,
20th June 1968

D 104368/31

SPECIFICATION AMENDED - SEE ATTACHED SLIP

excellent durability and does not wear off for a long period of time.

A further object of the invention is to provide a polytetrafluoroethylene coating composition producing a coating which has an ability to form thereon a new continuous phase of polytetrafluoroethylene by the action of spreading or melt-flowing caused by the local heating resulting from friction, whereby the durability, particularly the lubricity, of the coating is markedly improved.

A still further object of the invention is to provide a polytetrafluoroethylene coating composition which can be employed as a markedly improved agent for producing onto the substrate surface a coating of a high order of lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive properties.

The above and other objects are accomplished according to the present invention by dispersing particles of polytetrafluoroethylene waxes having a molecular weight of from 1,000 to 150,000 in a high molecular substance-containing solution having an ability to form a film when applied to the substrate surface by dipping, spraying, or brushing, and allowed to dry at a normal atmospheric temperature, namely, without the application of heat treatment to the resultant coating.

The coating thus obtained exhibits a high order of adherence to the substrate surface. The particles of polytetrafluoroethylene waxes employed are uniformly and discontinuously distributed throughout the surface layer and the intermediate layers of the coating. Said polytetrafluoroethylene particles are further firmly inlaid in the resin layers, so that the particles do not flake away. When the coating is subjected to rubbing or friction, the polytetrafluoroethylene wax particles present in the surface layer of the coating are forced to spread themselves throughout the outermost surface layer of the coating so as to form a continuous phase therein, whereby a high order of protective, lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive effects is obtained. Said continuous phase is also formed when the particles of polytetrafluoroethylene waxes present in the coating is melted by, for instance, repeated friction, and a high order of lubricity is thereby obtained when applied, for instance, to bearings and the like mechanical appliances. Said ability to form a continuous phase, further, is maintained for a long period of time when friction is continued, because a new continuous phase is formed one after another until the coating completely wears off.

The high molecular substance-containing solution employed in this invention includes

all of the solutions having an ability to form a film of the high molecular substance contained therein when dried at a normal atmospheric temperature, namely, solutions of high molecular substances, such as cellulose derivatives, polymers of ethylenically unsaturated compounds, and natural and synthetic rubbers. To raise the evaporating ability of the solution, there are employed organic solvents, such as having a specific evaporating rate in the order of from 0.1 to 20.0, preferably from 0.7 to 7.7, in terms of the evaporating velocity of 90 percent n-butyl acetate aqueous solution as 1. When an aerosol propellant is added to the coating compositions of this invention, there can be employed solvents of a lesser degree of evaporating ability.

The high molecular substance-containing solution employed in this invention is prepared by dissolving in an organic solvent a high molecular substance as specified before, and by diluting the resultant solution, where necessary. Desirable solvents and diluents for cellulose ethers, such as methyl cellulose and ethyl cellulose, are ethanol, isopropanol, n-butanol, and the like alcohols; acetone, methyl ethyl ketone and the like ketones; toluene, benzene, and the like aromatic compounds; and ethylene tetrachloride, methylene chloride, carbon tetrachloride, and the like haloalkanes and haloalkenes. Desirable solvents and diluents for cellulose esters, such as nitrocellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, and cellulose propionate, are acetone, diacetone alcohol, cyclohexanone, methyl acetate, ethyl lactate, methyl ethyl ketone, dioxane, methylene chloride, nitropropane, chloroform, ethylene dichloride, toluene, xylene, mineral spirits, butanol, and the like. Desirable solvents and diluents for polymers of ethylenically unsaturated compounds such as polyvinyl acetate, polyvinyl chloride, polystyrene, polyacrylic acid esters, vinyl chloride-vinyl acetate copolymer, vinyl acetate-acrylic acid esters copolymer, polymethacrylic acid esters, polyvinyl acetal and polyvinyl butyral, are ethyl acetate, butyl acetate, methanol, ethanol, benzene, cyclohexanone, tetrahydrofuran, toluene, xylene, aniline, chloroform, cresol, phenol, dioxane, ethylene glycol monoethers, and the like. Further, desirable solvents and diluents for rubber-like substances, such as Neoprene, nitrile rubbers and natural rubbers, are toluene, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, and the like. The above specified solvents and diluents are selected in accordance with the species of the high molecular substance to be employed and are used either singly or in combination with each other or one another.

The polyterephthaloylene waxes emulsion, isopropenol, cyclohexanol, and the like aliphatic alcohols; ethyl mercaptaan, di-methylidisulfide, and the like aliphatic propionaldehydes; acetone, methyl ketones, cyclohexane, and the like aliphatic ketones; aldehydes; acetate, ethyl acetate, and the like aliphatic esters, isolactic acid, and the like aliphatic acids; dimethyl phosphite, di-butyryl phosphite, and the like aliphatic compounds. The polyterephthaloylene waxes emulsion, isopropenol method, prepared by other known method comprising pyrolyzing at a temperature above 350°C. 30 or, Teflon 4IX. As compared with the polymer having a molecular weight less than 1,000,000 and which is placed on the market in the form of suspension under the market having a molecular weight more than 1,000,000 and which is placed in this invention can also be prepared by other known method comprising pyrolyzing at a temperature above 350°C. 35 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C. 40 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C. 45 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C. 50 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C. 55 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C. 60 The polyterephthaloylene waxes emulsion, isopropenol method, prepared by this invention can further be prepared by a method comprising pyrolyzing at a temperature above 350°C.

taining 4 percent of dimethylformamide and 0.1 percent of azobisisobutyronitrile in a reaction tower under 15 kg/cm² at 100° C. 3 Parts of the resultant telomer dispersion containing 25 percent of particles of polytetrafluoroethylene waxes having an average molecular weight of 3,000 were added with stirring until homogeneous to 7 parts of a solution consisting of 14 percent of 5 to 7 second nitrocellulose, 14 percent of dammar gum, 4 percent of dibutyl phthalate, 2 percent of cyclohexanone, 1 percent of β-ethoxyethanol, CH₃, CH₂, OCH₂, CH₃, OH, 2 percent of amyl acetate, 20 percent of butyl acetate, 19 percent of ethyl acetate, 6 percent of butanol, 7 percent of methanol, and 11 percent of benzene. The resultant composition was diluted with a mixture of 25 percent of ethyl acetate, 15 percent of butyl acetate, 4 percent of amyl acetate, 5 percent of butanol, 1 percent of β-ethoxyethanol, CH₃, CH₂, OCH₂, CH₂OH, and 50 percent of benzene, and applied by brushing to the running surfaces of skis, allowing the articles to dry at a room temperature (about 25° C.) for one hour. The resultant milk-white coating imparted a marked running ability to the skis.

Example 3

30 20 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 2 were blended with 100 parts of a mixture consisting of 5 percent of benzyl cellulose, 22 percent of Manila copal, 7 percent of benzene, 64 percent of methanol, and 2 percent of butylene glycol, and ball-milled for 50 hours until homogeneous. The coatings formed with the resultant composition at a room temperature (about 25° C.) exhibited a marked adherence to the substrate surface of wood, and the coefficient of static friction on glass plates was 0.030.

Example 4

45 20 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 2 and containing the particles of polytetrafluoroethylene waxes having an average molecular weight of 8,000 and m.p. 50 314° C. in the concentration order of 15 percent in carbon tetrachloride were blended until homogeneous with 100 parts of a mixture consisting of 1.43 part of polyvinyl acetate of an average polymerization degree of 300, 2.8 parts of butyl phthalate, 14.3 parts of methanol, 23.6 parts of ethyl acetate, 7.1 parts of butyl acetate, and 42.8 parts of benzene. The resultant composition was applied to rubber rings and dried 60 at a room temperature (about 25° C.) for one hour, forming a coating excelled in slidability for valves.

Example 5

65 30 Parts of the polytetrafluoroethylene dispersion prepared in accordance with

Example 4 were added with stirring until homogeneous to 100 parts of a solution consisting of 10 parts of an 87:13 molar vinyl chloride-vinyl acetate copolymer having an average molecular weight of 70 100,000 3 parts of diethylphthalate, 50 parts of benzene, 20 parts of acetone, and 25 parts of ethyl acetate. The resultant composition formed a coating at a room temperature (about 25° C.) exhibiting a marked 75 adherence to the articles treated therewith.

Example 6

10 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 4 were blended with stirring until 80 homogeneous with a mixture consisting of 10 parts of polystyrene having an average polymerization degree of 350, 2.5 parts of tricresyl phosphate, and 77.5 parts of benzene. The resultant composition formed a 85 coating at a room temperature (about 25° C.) particularly excelled in water-repellency and in durability at low temperatures.

Example 7

30 Parts of the polytetrafluoroethylene 90 dispersion prepared in accordance with Example 4 were blended with stirring until homogeneous with 100 parts of a mixture consisting of 5 parts of vinyl butyrol resin, 5 parts of 1/2 second nitrocellulose, 7 parts 95 of butyl acetate, 20 parts of ethyl acetate, 44 parts of tricresyl phosphate, 20 parts of ethanol, 31 parts of benzene, 6 parts of butanol, and 2 parts of cyclohexane. The resultant composition formed at a room 100 temperature (about 25° C.) a coating particularly excelled in adherence to metals.

Example 8

50 Parts of polytetrafluoroethylene 105 dispersion prepared in accordance with Example 4 were blended with stirring until homogeneous with 100 parts of a mixture consisting of 3 parts of carbon black, 15 parts of nitrocellulose, 5 parts of dibutyl phthalate, 30 parts of ethyl acetate, 9 parts of butanol, and 15 parts of n-butyl acetate. The resultant composition formed at a room 110 temperature (about 25° C.) a dark coating excelled in lubricity.

Example 9

6.5 Parts of polytetrafluoroethylene wax particles having an average size of 250 microns, an average molecular weight of 2,000, and m.p. 276° C. were admixed with 120 stirring with a solution consisting of 6.5 parts of 5 second R. S. type nitrocellulose, 18 parts of zinc stearate, 3 parts of magnesium carbonate, 2.5 parts of castor oil, 16 parts of ethyl acetate, 6 parts of butyl acetate, and 16 parts of denatured alcohol, and ball-milled for 24 hours. 100 Parts of the resultant composition were then filled in an aerosol bomb in admixture with 200 parts of a 15:85 (weight ratio) 125

Parts of the resultant composition were then filled in an aerosol bomb in admixture with 200 parts of a 15:85 (weight ratio) 130

ployed in this invention can still further be prepared by a process comprising continuously supplying to a reaction tower a solution consisting of a radical initiator 5 dissolved in a telogen in conjunction with tetrafluoroethylene gas under a pressure of from 1 to 15 kg/cm². During the course of this reaction, there is evacuated from the top of the reaction tower the mixture containing formed telomers, unreacted tetrafluoroethylene, and excess telogen to isolate by condensation the formed telomers in the state of being dispersed in excess telogen from the unreacted tetrafluoroethylene. This 10 continuous process has an advantage of easily controlling the reaction conditions and the distribution of molecular weight of the telomers formed. The reaction proceeds without accompanying any dangerous handling. The telogen and radical initiator employed in this process are identical with those substances employed in the conventional telomerization method as specified before. The above instances as specified 15 hereinbefore, however, are illustrative only and do not necessarily limit the manufacturing method of the polytetrafluoroethylene waxes employed in this invention.

The coating compositions of this invention desirably contain polytetrafluoroethylene particles as fine as possible. To prepare said compositions, in the first place, the polytetrafluoroethylene waxes prepared in accordance with any of the aforespecified processes are pulverized into particles 20 of a size of less than 100 microns, preferably less than 20 microns, and then dispersed in the high molecular substance-containing solution. In the second place, the particles of said polytetrafluoroethylene waxes having a relatively high order of particle size, such as from 100 to 500 microns, are ball-milled in conjunction with the high molecular substance-containing solution. In the third place, more desirable effects 25 can be obtained by dispersing the particles of said polytetrafluoroethylene waxes in an organic dispersing medium, and then adding the resultant dispersion containing polytetrafluoroethylene particles of less than 100 microns with the high molecular substance-containing solution. Said organic dispersing medium includes those organic 30 dispersants which do not allow the solid ingredients to coagulate or precipitate when said polytetrafluoroethylene particles-containing dispersion is admixed with the high molecular substance-containing solution. It 35 is further desirable that said organic dispersing medium is identical with the solvents for the high molecular substance to be employed thereafter. In case the organic dispersing medium which is not identical 40 with the solvent for the high molecular sub-

stance is employed for dispersing the particles of said polytetrafluoroethylene waxes, the amount of the polytetrafluoroethylene dispersion to be admixed with the high molecular substance-containing solution 70 should be limited to such an extent as not to allow the solid ingredients to coagulate or precipitate. The amount of said polytetrafluoroethylene dispersion, however, can be increased when a solvent having a high 75 order of solubility for high molecular substances is employed as a medium for dissolving the high molecular substance to be employed, or when there is added a subsidiary or an auxiliary solvent to the high 80 molecular substance-containing solution. In the fourth place, when the polytetrafluoroethylene waxes to be employed in this invention are manufactured by telomerization, the resultant dispersion which is obtained 85 by separating out the unreacted tetrafluoroethylene and contains in the excess telogen the polytetrafluoroethylene particles of less than 100 microns, is advantageously admixed by itself, namely, without isolating the polytetrafluoroethylene particles from the excess telogen, in the high molecular substance-containing solution. The above 90 specified instances described hereinbefore, however, are illustrative only and not limiting the process for preparing the coating compositions of this invention.

The order of concentration of the coating compositions of this invention varies in accordance with the modes of application, such as dipping, brushing, or spraying. Said coating compositions, however, are usually employed in the order of total solid concentration of from 0.1 to 30 percent by weight, the term 'total solid' being employed 100 to imply the total amount of the polytetrafluoromethylene particles and high molecular weight polymeric material present in the coating composition of this invention. The most desirable effects are obtained 110 when the coating composition of this invention is prepared by confining the total solids present in the composition to the extent of from 20 to 30 percent by weight, and the resultant composition is employed 115 by diluting, where necessary, in accordance with the modes of application as specified before.

The composition ratio of the polytetrafluoroethylene particles present in the coating compositions of this invention ranges from 1 to 99 percent, preferably from 15 to 85 percent for best results, by weight of the total solids present in the coating composition.

There can be added to the coating compositions of this invention a suitable filler and/or diluent. The amount and species of these additives should be carefully determined not to allow the solid contents pre- 125 130

